

Welcome to course 28140

## Introduction to Chemical Reaction Engineering

Fall semester 2017

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Department of Chemical & Biochemical Engineering  
Technical University of Denmark

## Lecture 1

Contents (text book p. 1-26, 69-99)

- Information and administrative matter
- Introduction
- Reactor types
- Mole balances for ideal reactors
- Kinetics and rate expressions
- Example: n'th order reaction in a constant volume batch reactor – use of Maple

## Course elements

- Lectures (5A) from 8.00 to ~10.00
  - Building 210 room 162
- Calculation session (5A) from ~10.00 to 12.00 (b210/152+162)
- Homework (hand in the following week, returned corrected)
- Four hour written exam: 21. December 2017
- Grading based on written exam and homework
- Assistant teacher for calculation sessions:  
Steen Müller Christensen,  
Ph.D. student



## Course material

- Text book: Elements of Chemical Reaction Engineering  
by H.S. Fogler, 5th edition
- All lecture slides, notes, exercises and  
solution to exercises will be posted on campusnet
- Use of the program Maple:  
The program may be downloaded from the homepage  
<http://www.gbar.dtu.dk/software/>

## Why study Chemical Reaction Engineering (CRE)?

- It distinguishes chemical engineers from others
- It is the heart of producing all chemicals
- It provides the necessary knowledge for safe and efficient operation of chemical plants
- Chemical reactions are the basis for all living systems
- Its principles applies to many areas:
  - Petroleum and chemical/biochemical/pharmaceutical industry
  - Living systems (fermentation, pharmacokinetics etc)
  - Environmental engineering (waste treatment, pollution reduction)
  - Semiconductor industry
  - Combustion
  - Engines
  - ...

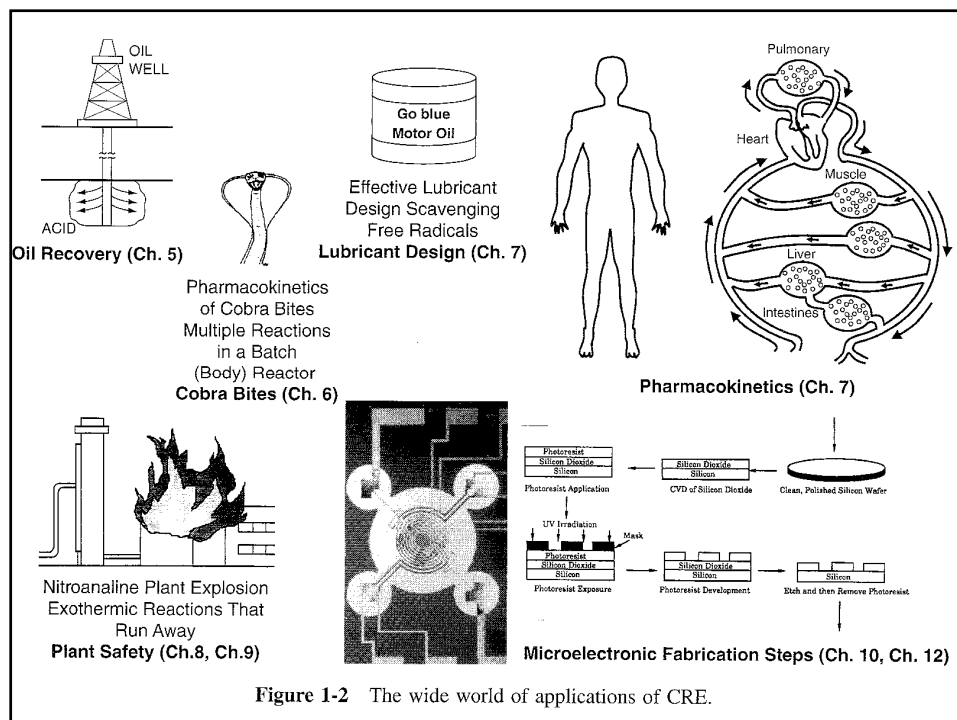


Figure 1-2 The wide world of applications of CRE.

## Industrial examples (I)

### Production of Synthesis Gas - Reforming

- Synthesis gas: A mixture of CO and H<sub>2</sub>
- Is produced from reaction of natural gas/oil by reaction with H<sub>2</sub>O and O<sub>2</sub>:
 
$$\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$$

$$\text{CH}_4 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{CO} + 2\text{H}_2$$

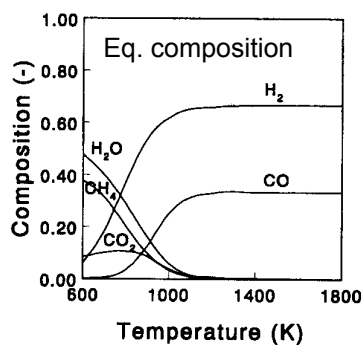
$$\text{CH}_4 + 2\text{O}_2 \rightleftharpoons \text{CO}_2 + 2\text{H}_2\text{O}$$

$$\text{CO} + \text{H}_2\text{O} \rightleftharpoons \text{CO}_2 + \text{H}_2$$
- Synthesis gas is applied for the production of many bulk chemicals such as methanol, ammonia, hydrogen, liquid fuels (gasoline and methanol), formic and acetic acid

## Industrial examples (I)

### Production of Synthesis Gas

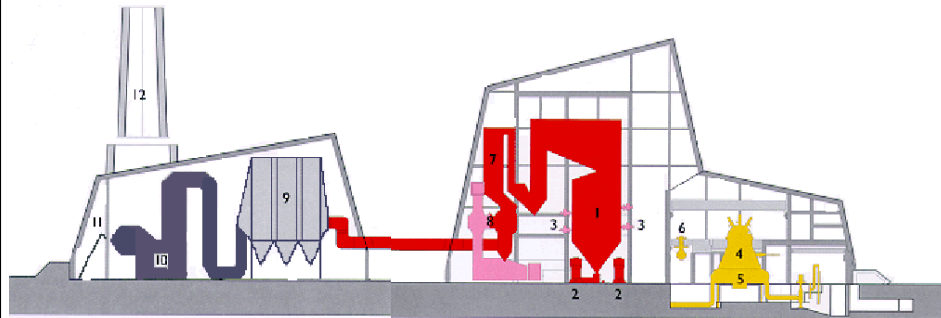
Auto-thermal reforming reactor: Initial sub-stoichiometric combustion followed by a catalytic conversion in a packed bed.



## Industrial examples (II)

### Power plant for combustion of gas/oil/coal/biomass

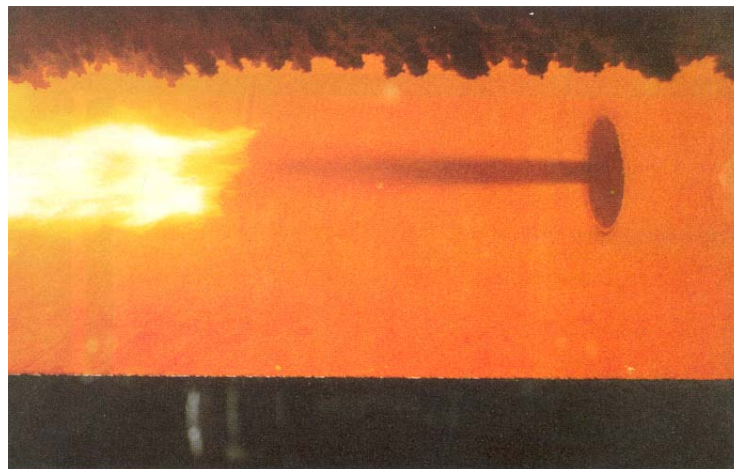
- |                      |                     |
|----------------------|---------------------|
| 1. Boiler (reactor)  | 7. DeNOx reactor    |
| 2. Mills             | 8. Air preheater    |
| 3. Burners           | 9. Electro filter   |
| 4. Turbine/generator | 10. Desulfurization |
| 5. Condensator       | 11. Gypsum storage  |
| 6. Feed water pump   | 12. Chimney         |



## Industrial examples (II)

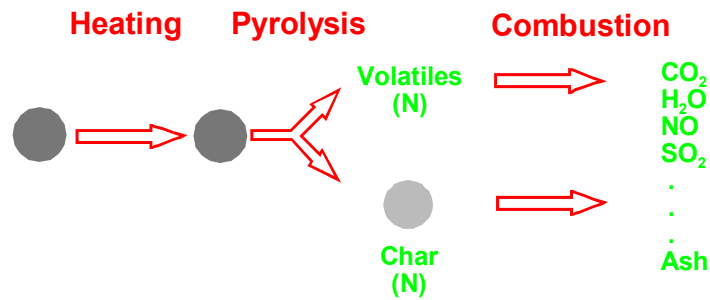
### Power plant for combustion of gas/oil/coal/biomass

#### Coal or biofuel dust flame



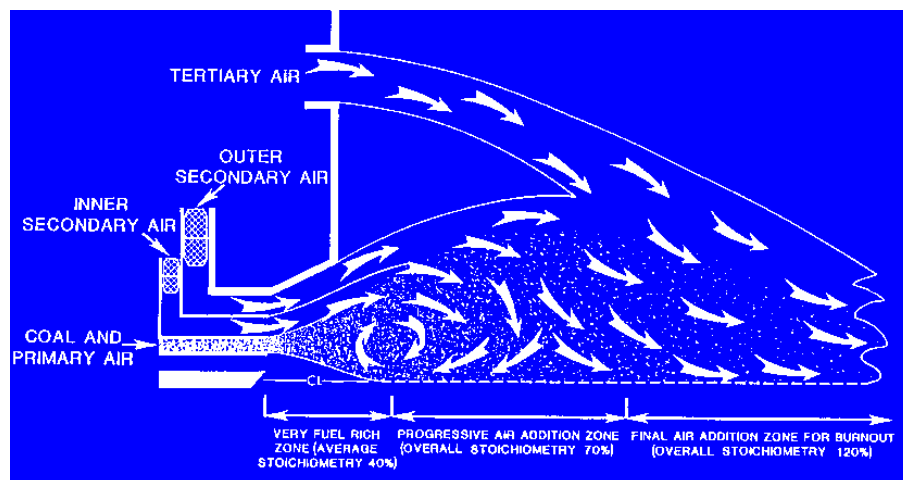
## Industrial examples (II)

Power plant for combustion of gas/oil/coal/biomass  
Schematic reactions in the flame



## Industrial examples (II)

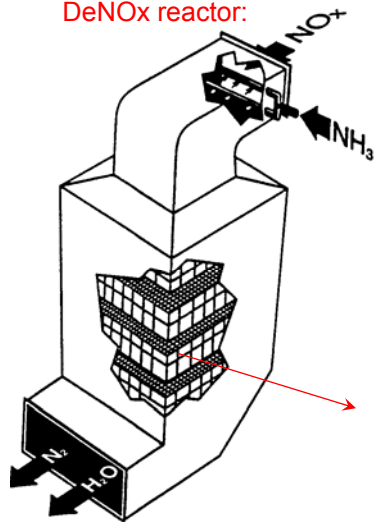
Power plant for combustion of gas/oil/coal/biomass  
Mixing in the near burner zone of a coal flame



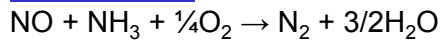
## Industrial examples (II)

Power plant for combustion of gas/oil/coal/biomass

DeNOx reactor:



Main reaction:



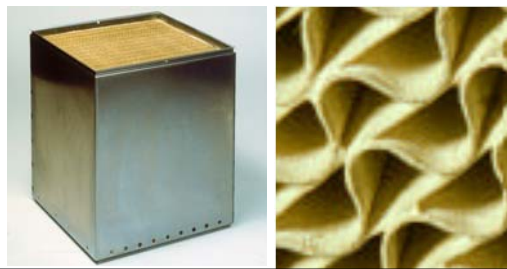
Characteristics:

Catalyst:  $\text{V}_2\text{O}_5/\text{WO}_3$  on a  $\text{TiO}_2$  carrier

Operating temperature: 300-400 °C

NOx-reduction: 80-90 %

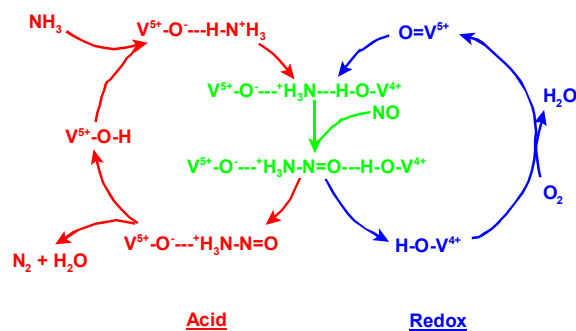
Life time: 3-5 years by HD coal comb.



## Industrial examples (II)

Power plant for combustion of gas/oil/coal/biomass

DeNOx mechanism:



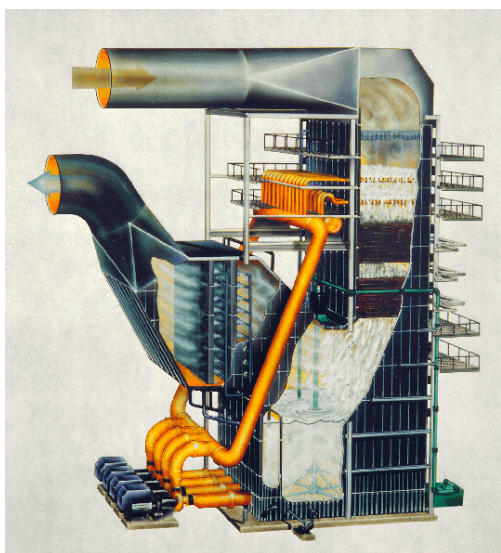
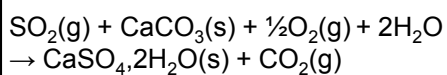
Derived rate expression: 
$$-r'_{\text{NO}} = k \cdot C_{\text{NO}} \cdot \frac{K_{\text{NH}_3} \cdot C_{\text{NH}_3}}{1 + K_{\text{NH}_3} \cdot C_{\text{NH}_3}}$$

## Industrial examples (II)

Power plant for combustion of gas/oil/coal/biomass

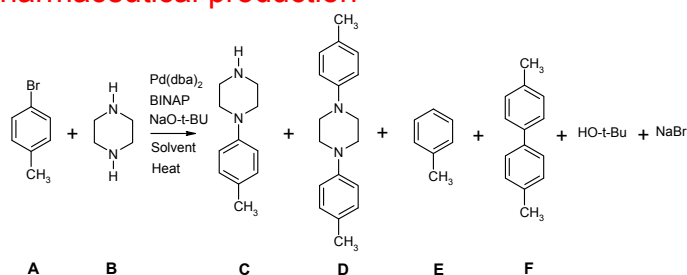
Desulfurization:

Three-phase slurry reactor:



## Industrial examples (III)

Pharmaceutical production

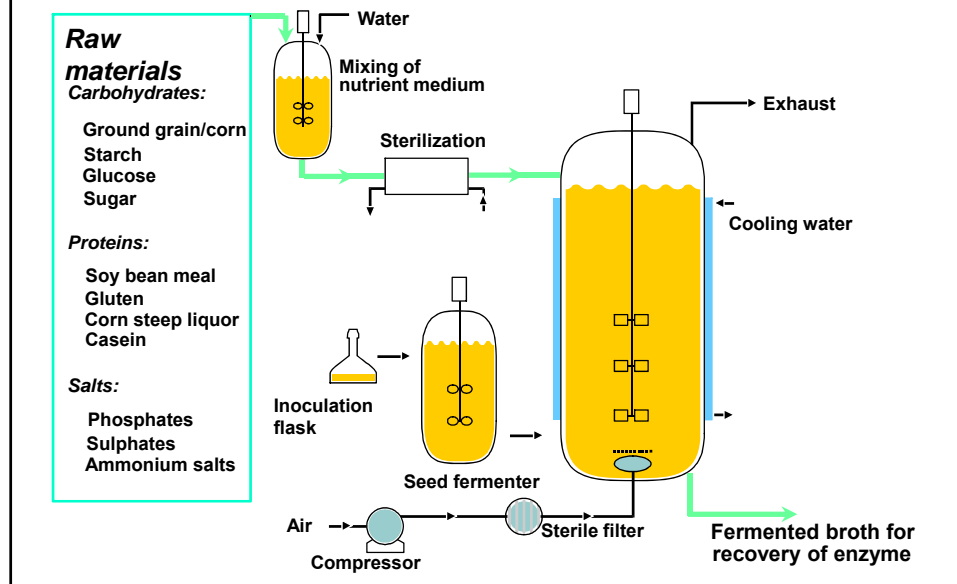


- Buchwald-Hartwig amination reaction
  - Desired product: **C**
  - Unwanted side products: **D**, **E** and **F**
- Concerning the reaction:
  - Homogeneous catalyst
  - Product distribution is affected by the ratio of **A** and **B**, but also the solvent plays a role. Especially in the formation of **E**.



## Industrial examples (IV)

### Fermentation: Biological production of e.g. enzymes



## Learning objectives of the course

A student who has met the objectives of the course will be able to:

- Explain the difference between rate expressions for elementary reactions and non-elementary reactions
- Explain the principles of the ideal reactor models: plug flow reactor, continuously stirred tank reactor, ideally stirred batch reactor
- Design optimal reactor configuration for reactor chains
- Set up and solve mathematical models for the ideal reactors under isothermal conditions for a single reaction, and for multiple reactions
- Set up and solve mole balances for other reacting systems than the three ideal reactor types
- Set up and solve mathematical models for bio-reactors
- Set up the energy balance for the ideal reactor types for single and multiple reactions with and without cooling
- Calculate the equilibrium conversion for a single reaction for isothermal and non-isothermal reactions
- Explain how multiple steady states occur in stirred reactors
- Design reactors for optimum and safe operation
- Set up and solve mathematical models for diffusion and reaction in porous catalyst pellets and calculate the effectiveness factor

## Learning objectives

By the end of today (incl. homework) you should:

- Be able to describe the working principle of the three ideal reactors types (ideally stirred batch reactor, ideal CSTR, plug flow reactor)
- Be able to derive the design equations (mole balances) for these reactors
- Be able to describe the difference between elementary and non-elementary reactions
- Write down the expression for an Arrhenius rate constant
- Be able to use Maple for solving simple algebraic equations and ODE's and plotting the results

## Types of reactions

- Homogeneous phase reactions:
  - Gas phase reaction
  - Liquid phase reaction
- Heterogeneous two-phase reactions:
  - Gas phase reaction catalyzed by a solid catalyst
  - Gas-solid reaction
  - Liquid phase reaction catalyzed by a solid catalyst
  - Liquid-liquid (immiscible) phase reaction
  - Gas-liquid phase reaction
- Heterogeneous three-phase reactions:
  - Gas-liquid-solid reaction

# Batch Reactors

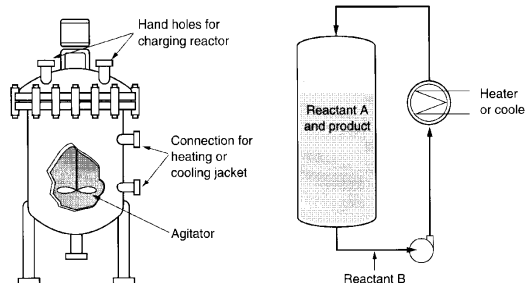


Figure 1-5(a) Simple batch homogeneous reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

Semibatch reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

Represent by:

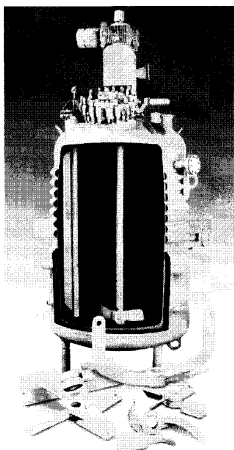
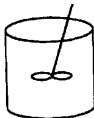


Figure 1-7(a) CSTR/batch reactor. (Courtesy of Pfaudler, Inc.)

## Batch reactors

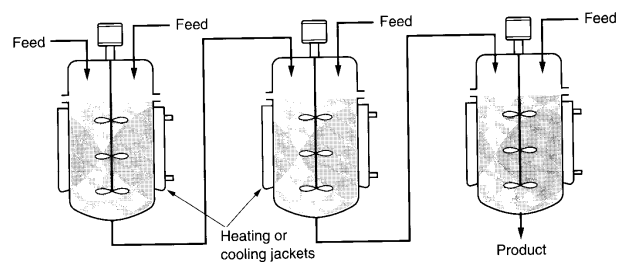
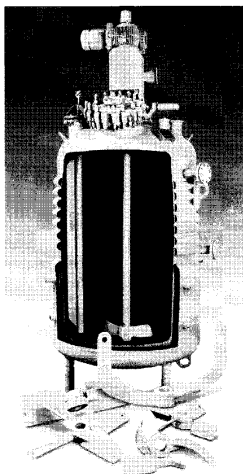
Pharmaceutical production – Batch reactors at Lundbeck



## Why Batch Reactors

- It is used for:
  - Small scale operations
  - Intermediate or one shot production/testing new processes
  - Pharmaceutical/Fermentation
  - Gas/Liquid/Liquid-Solid phase reaction
- Advantage:
  - High conversion
  - Operational flexibility
- Disadvantage:
  - High labor cost
  - Product quality may vary
  - Difficult to achieve large scale production

## Continuous Stirred Tank Reactor (CSTR)



Battery of stirred tanks. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

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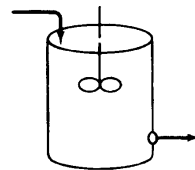


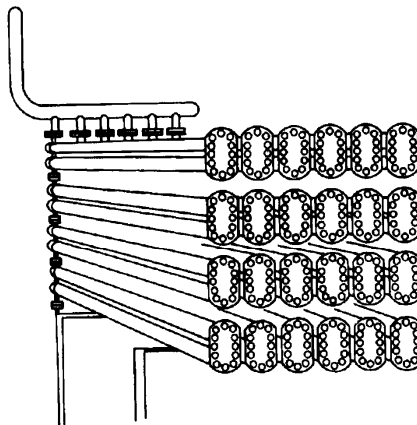
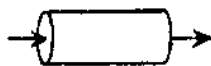
Figure 1-7(a) CSTR/batch reactor. (Courtesy of Pfaudler, Inc.)

## Why CSTR

- It is used for:
  - Processes requiring agitation
  - Mostly liquid phase reactions
- Advantage:
  - Continuous operation (normally operated at steady state)
  - Good temperature control
  - Low cost
- Disadvantage:
  - Low conversion of reactants

## Tubular Reactors (Plug Flow Reactors (PFR))

Represent by:

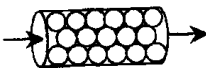


**Figure 1-8(a)** Longitudinal tubular reactor. [Excerpted by special permission from *Chem. Eng.*, 63(10), 211 (Oct. 1956). Copyright 1956 by McGraw-Hill, Inc., New York, NY 10020.]

## Why Tubular Reactors

- It is used for:
  - Gas phase reactions
  - Large scale, fast reactions
- Advantage:
  - Continuous operation
  - Relatively easy to maintain
  - High conversion (the highest of all reactors types)
  - Low operating cost
- Disadvantage:
  - Difficult to control temperature

## Other Reactors

- Semibatch:
  - Typically one reactant is charged initially and the other is fed continuously
- Tubular fixed (packed) bed reactor: 
  - Tubular reactor packed with catalyst particles
- Fluidized bed reactor:
  - Catalyst particles are fluidized by the reaction mixture flowing upwards through the fluidized particles
- Transport reactors:
  - Catalyst/solid reactant particles are entrained by the reaction mixture

## Some more reactors (I)

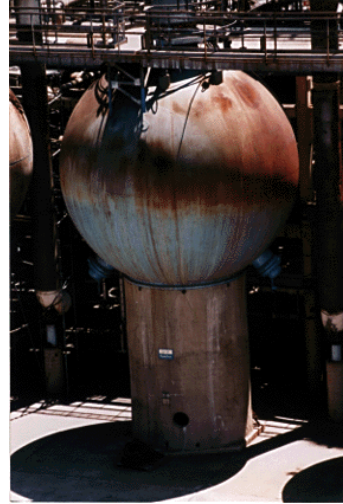
### Packed bed catalytic reactors

Reactor system in oil industry



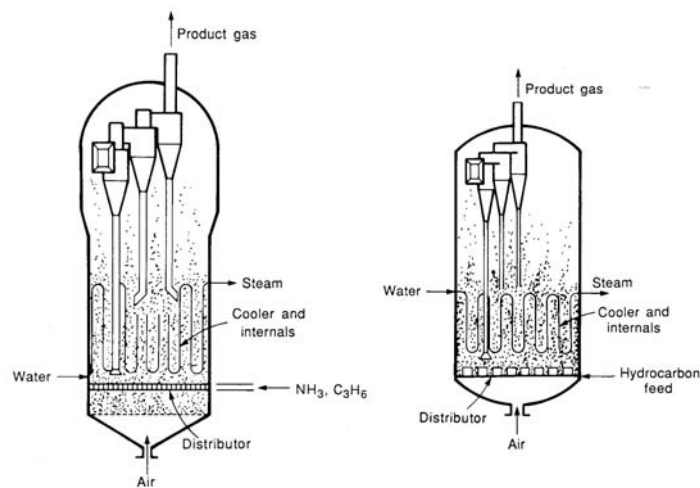
### Spherical reactor

Paraffin  $\rightarrow$  aromatic +  $H_2$



## Some more reactors (II)

### Fluidized bed catalytic reactors for exothermic reactions



Acrylonitrile

Maleic anhydride

## The pillars of CRE

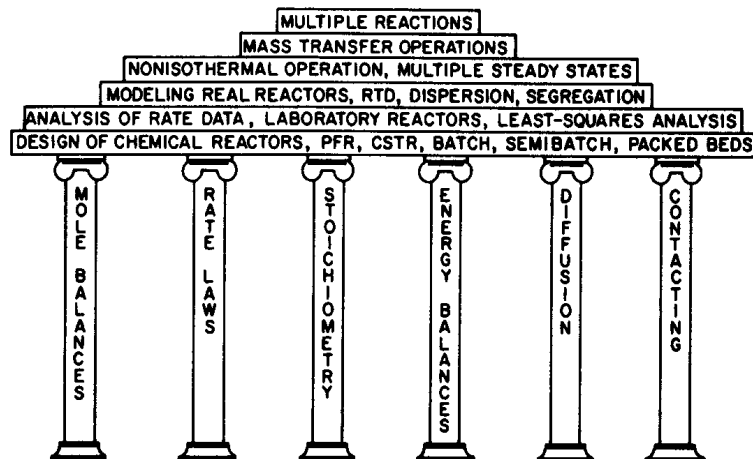


Figure P-1 Pillars of Chemical Reaction Engineering.

## General mole balances (I)

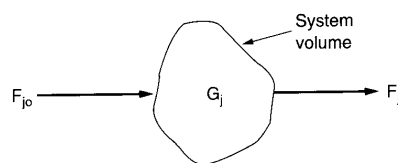


Figure 1-3 Balance on system volume.

A mole balance on species  $j$  at any instant in time,  $t$ , yields the following equation:

$$\begin{array}{ccccccc}
 \left[ \begin{array}{c} \text{rate of flow} \\ \text{of } j \text{ into} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] & + & \left[ \begin{array}{c} \text{rate of generation} \\ \text{of } j \text{ by chemical} \\ \text{reaction within} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] & - & \left[ \begin{array}{c} \text{rate of flow} \\ \text{of } j \text{ out of} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] & = & \left[ \begin{array}{c} \text{rate of} \\ \text{accumulation} \\ \text{of } j \text{ within} \\ \text{the system} \\ \text{(moles/time)} \end{array} \right] \\
 \text{in} & + & \text{generation} & - & \text{out} & = & \text{accumulation} \\
 F_{j0} & + & G_j & - & F_j & = & \frac{dN_j}{dt} \quad (1-3)
 \end{array}$$



## General mole balances (II)

$$F_{j0} + G_j - F_j = \frac{dN_j}{dt} \quad r_j = \frac{\text{moles J generated}}{\text{volume} \cdot \text{time}}$$

Express  $G_j$  in terms of reaction rate:

In a volume element  $\Delta V_1$ , we have:  $\Delta G_{j1} = r_{j1} \cdot \Delta V_1$

Sum over all  $\Delta V_i$ :

$$G_j = \sum_{i=1}^M \Delta G_{ji} = \sum_{i=1}^M r_{ji} \cdot \Delta V_i$$

For  $\Delta V_i \rightarrow dV_i$  we have:

$$G_j = \int^V r_j \cdot dV \Rightarrow$$

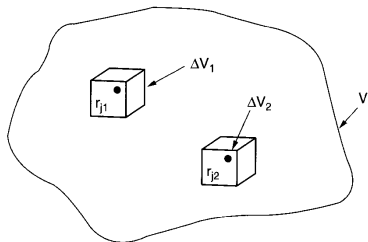
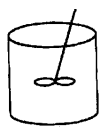


Figure 1-4 Dividing up the system volume  $V$ .

$$F_{j0} - F_j + \int^V r_j \cdot dV = \frac{dN_j}{dt}$$

## Mole balance for batch reactor (I)



$$F_{j0} - F_j + \int^V r_j \cdot dV = \frac{dN_j}{dt}$$

$$F_{j0} = F_j = 0 \Rightarrow$$

$$\int^V r_j \cdot dV = \frac{dN_j}{dt}$$

If there is no spatial variation of reaction rate (perfectly mixed):

$$\frac{dN_j}{dt} = r_j \cdot V \quad \text{or} \quad \frac{1}{V} \frac{dN_j}{dt} = r_j \quad \text{or} \quad t_1 = \int_{N_{A0}}^{N_{A1}} \frac{dN_A}{r_A V}$$

## Mole balance for batch reactor (II)

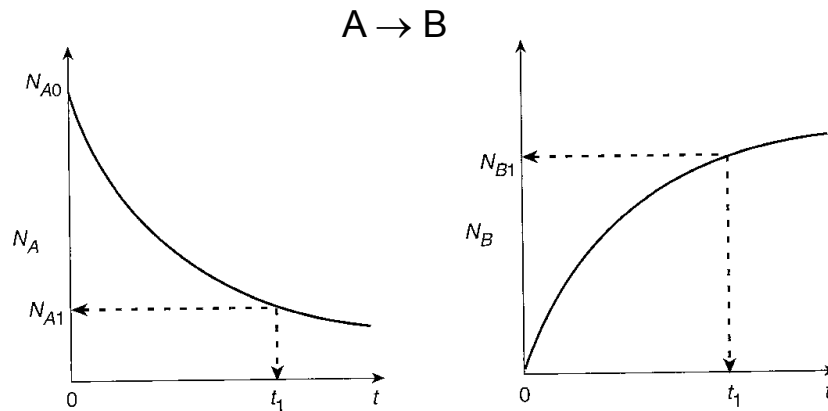
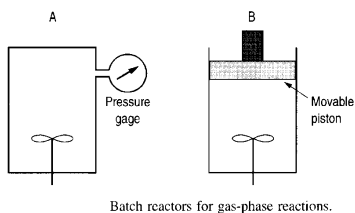


Figure 1-6 Mole-time trajectories.

## Mole balance for batch reactor (III)

Constant volume or constant pressure



General mole balance equation:

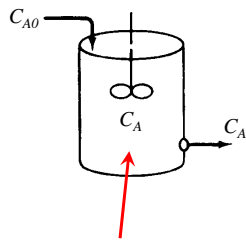
$$\frac{1}{V} \frac{dN_A}{dt} = r_A$$

Constant volume: 
$$\frac{1}{V} \frac{dN_A}{dt} = \frac{d(N_A/V)}{dt} = \frac{dC_A}{dt} = r_A$$

Constant pressure:  
(non-constant volume) 
$$\frac{1}{V} \frac{dN_A}{dt} = \frac{1}{V} \frac{d(C_A \cdot V)}{dt} = \frac{dC_A}{dt} + \underbrace{\frac{C_A}{V} \frac{dV}{dt}}_{\text{New term}} = r_A$$

It does make a difference !

## Mole balance for CSTR (I)

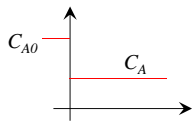


$$F_{j0} - F_j + \int^V r_j \cdot dV = \frac{dN_j}{dt}$$

Steady state in CSTR:  $\frac{dN_j}{dt} = 0 \Rightarrow$

Same concentration everywhere

$$F_{j0} - F_j + \int^V r_j \cdot dV = 0$$



No spatial variation of reaction rate:

$$F_{j0} - F_j + r_j \cdot V = 0 \quad \text{or} \quad V = \frac{F_{j0} - F_j}{-r_j}$$

## Mole balance for CSTR (II)

$v$ : Volumetric flow rate [ $\text{m}^3/\text{s}$ ]

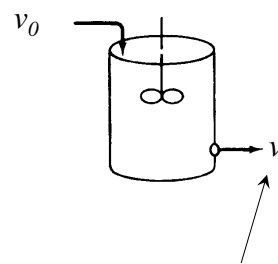
$$F_{j0} = v_0 \cdot C_{j0} \quad ; \quad F_j = v \cdot C_j$$

If the volumetric flow rate is constant  $v_0 = v$  then:

$$V = \frac{F_{j0} - F_j}{-r_j} = \frac{v_0 \cdot (C_{j0} - C_j)}{-r_j} \Rightarrow$$

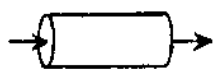
$$\tau \equiv \frac{V}{v_0} = \frac{(C_{j0} - C_j)}{-r_j}$$

$\tau$  = Space Time [s];  $1/\tau$  is called Space Velocity (SV)



$v$  may have changed from  $v_0$

## Mole balance for PFR (I)



$$F_{j0} - F_j + \int_V^V r_j \cdot dV = \frac{dN_j}{dt}$$

Steady state in PFR:  $\frac{dN_j}{dt} = 0$

$$\Delta G_j = \int_V^{V+\Delta V} r_j dV = r_j \Delta V$$

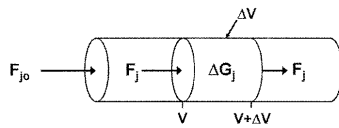


Figure 1-10 Mole balance on species  $j$  in volume  $\Delta V$ .

Consider  $\Delta V$ :

$$F_j(V) - F_j(V + \Delta V) + r_j \cdot \Delta V = 0$$

$\Downarrow$

$$\frac{F_j(V + \Delta V) - F_j(V)}{\Delta V} = r_j \Rightarrow \Delta V \rightarrow 0$$

$$\boxed{\frac{dF_j}{dV} = r_j \quad \text{or} \quad V = \int_{F_{j0}}^{F_j} \frac{dF_j}{r_j}}$$

## Mole balance for PFR (II)

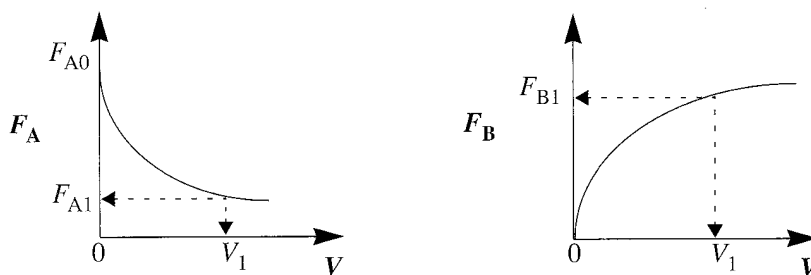
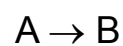


Figure 1-12 Profiles of molar flow rates in a PFR.

## Mole balance for PFR (II)

Tubular reactor with constant cross sectional area,  $A$

$$\frac{dF_j}{dV} = \frac{dF_j}{d(A \cdot y)} = r_j \Rightarrow \frac{1}{A} \frac{dF_j}{dy} = r_j$$


Constant volumetric flow rate  $v = v_0$

$$\frac{dF_j}{dV} = \frac{d(v_0 \cdot C_j)}{dV} = \frac{dC_j}{d(V/v_0)} = r_j \Rightarrow$$

$$\frac{dC_j}{d\tau} = r_j \quad ; \quad \tau = V/v_0 \text{ is the space time}$$

Note: The mole balance for batch and PFR becomes identical

## Mole balance for Packed Bed Reactor



$$F_{j0} - F_j + \int^V r_j \cdot dV = \frac{dN_j}{dt}$$

Steady state in PFR:  $\frac{dN_j}{dt} = 0$ ;  $r'_j = \frac{\text{moles J generated}}{\text{kg catalyst} \cdot \text{time}}$

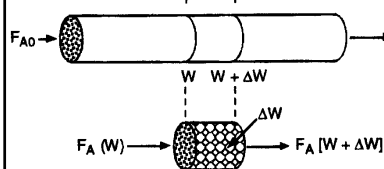


Figure 1-14 Packed-bed reactor schematic.

$$F_j(W) - F_j(W + \Delta W) + r'_j \cdot \Delta W = 0$$




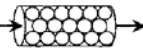
$\Downarrow$

$$\frac{F_j(W + \Delta W) - F_j(W)}{\Delta W} = r'_j \Rightarrow \Delta W \rightarrow 0$$

$$\frac{dF_j}{dW} = r'_j \quad \text{or} \quad W = \int_{F_{j0}}^{F_j} \frac{dF_j}{r'_j}$$

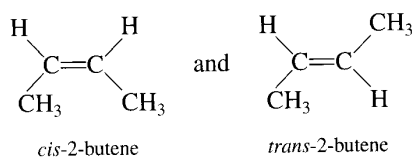
## Overview of mole balances, p. 24 HSF

TABLE S-1 SUMMARY OF REACTOR MOLE BALANCES

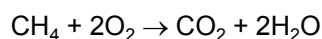
Reactor	Comment	Mole Balance Differential Form	Algebraic Form	Integral Form
	Batch	No spatial variations	$\frac{dN_A}{dt} = r_A V$	$t_1 = \int_{N_{A1}}^{N_{A0}} \frac{dN_A}{-r_A V}$
	CSTR	No spatial variations, steady state	—	$V = \frac{F_{A0} - F_A}{-r_A}$
	PFR	Steady state	$\frac{dF_A}{dV} = r_A$	$V_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r_A}$
	PBR	Steady state	$\frac{dF_A}{dW} = r'_A$	$W_1 = \int_{F_{A1}}^{F_{A0}} \frac{dF_A}{-r'_A}$

## Chemical Reactions

- Chemical species involved in a reaction system:  
The identity of a chemical species is determined by the kind, number and configuration of that species' atoms



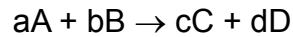
- Chemical reaction: A detectable number of molecules of one or more species have lost their identity and assumed a new identity:



- Types of chemical reactions:
  - Decomposition:  $\text{N}_2\text{O} \rightarrow \text{N}_2 + \frac{1}{2}\text{O}_2$
  - Combination:  $\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$
  - Isomerization:  $\text{cis-2-butene} \rightarrow \text{trans-2-butene}$

## Stoichiometry and Reaction Rate

- Stoichiometry:



- Relation between reaction rates:

$$R = \frac{-r_A}{a} = \frac{-r_B}{b} = \frac{r_C}{c} = \frac{r_D}{d}$$

- Definition of reaction rate:

$$r_A = \frac{dC_A}{dt}$$

- How can reaction rates be measured ?:

Constant volume batch reactor:  $r_A = \frac{dC_A}{dt}$

CSTR:  $r_A = -\frac{F_{A0} - F_A}{V}$

## Units of Reaction Rate

$$r_j = \frac{\text{moles J generated}}{(\text{fluid volume}) \cdot \text{time}}$$

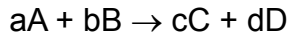
$$r_j' = \frac{\text{moles J generated}}{(\text{mass of solid}) \cdot \text{time}}$$

$$r_j'' = \frac{\text{moles J generated}}{(\text{surface area}) \cdot \text{time}}$$

$$r_j''' = \frac{\text{moles J generated}}{(\text{volume of solid}) \cdot \text{time}}$$

$$r_j'''' = \frac{\text{moles J generated}}{(\text{volume of reactor}) \cdot \text{time}}$$

## Reaction Rate Constant & Rate Laws



- Reaction rate depends on:
  - Temperature
  - Concentration of reacting species
$$-r_A = k_A(T) f(C_A, C_B, \dots)$$
- Rate law:  $f(C_A, C_B, \dots)$
- Specific reaction rate (constant),  $k_A(T)$ :
  - $k_A(T) = A e^{-E/RT}$  (Arrhenius expression)
  - $A$  = Preexponential factor/frequency factor
  - $E$  = Activation energy [J/mol]
  - $R$  = Gas constant = 8.3144 [J/(mol K)]
  - $T$  = Absolute temperature [K]

## Reaction Rate Constant & Rate Laws

- Specific reaction rate (constant),  $k_A(T)$ :

$$k_A(T) = A \cdot e^{-E/RT} \Rightarrow$$

$$\ln k_A = \ln A - \frac{E}{R} \cdot \frac{1}{T}$$

- Straight line in a  $\ln(k)$  versus  $1/T$  plot

- In terms of  $k_A(T_0)$

$$k_A(T) = k_A(T_0) \cdot \exp \left[ \frac{E}{R} \cdot \left( \frac{1}{T_0} - \frac{1}{T} \right) \right]$$

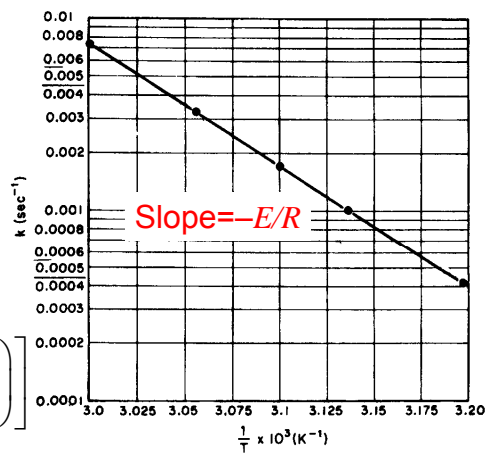
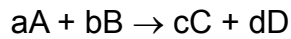


Figure E3-1.2



## Reaction Order



- Reaction order (power law expression)

$$-r_A = k_A \cdot C_A^\alpha C_B^\beta$$

- The reaction order w.r.t. A is  $\alpha$
- The reaction order w.r.t. B is  $\beta$
- The overall reaction order is  $\alpha + \beta$
- Zero-order reaction:  $-r_A = k_A; [k_A] = \text{mol}/(\text{m}^3 \cdot \text{s})$
- First-order reaction:  $-r_A = k_A \cdot C_A; [k_A] = \text{s}^{-1}$
- Second-order reaction:  $-r_A = k_A \cdot C_A^2; [k_A] = \text{m}^3/(\text{mol} \cdot \text{s})$

## Elementary Reactions

A reaction follows an **elementary rate law** if the reaction order of each species is identical with the stoichiometric coefficient of the reaction as written:



$$-r_A = k_A \cdot C_A^a \cdot C_B^b$$

## Non-Elementary Reactions (II)

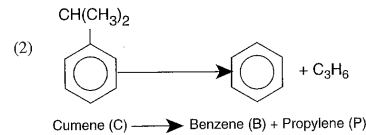
TABLE 3-1. EXAMPLES OF REACTION RATE LAWS (CONTINUED)

### C. Nonelementary Rate Laws

**Gas phase reaction** (1)  $\text{CH}_3\text{CHO} \longrightarrow \text{CH}_4 + \text{CO}$

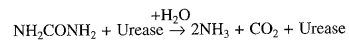
$$-r_{\text{CH}_3\text{CHO}} = kC_{\text{CH}_3\text{CHO}}^{3/2}$$

**Catalytic gas phase reaction**



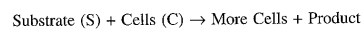
$$-r_c = \frac{k[(P_c - P_B P_P)K_P]}{1 + K_B P_B + K_C P_C}$$

### D. Enzymatic Reactions (Urea (U) + Urease (E))



$$-r_U = \frac{kC_U}{K_M + C_U}$$

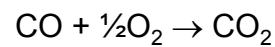
### E. Biomass Reactions



$$-r_U = \frac{kC_S C_C}{K_S + C_S}$$

## Non-Elementary Reactions (I)

Most reactions are non-elementary, i.e. there are underlying elementary reactions, for example:



- see next slide

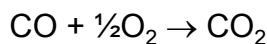
TABLE III  
CO/H<sub>2</sub>/O<sub>2</sub> Reaction Mechanism, Reaction rates in cm<sup>3</sup>-mole-sec-kcal-K units,  $k = AT^n \exp(-E_a/RT)$

	$\Delta H_{298.15}$	$\log(A_i)$	$n_i$	$E_{a,i}$	$UF$	$T_{\text{range}}$ (K)	Reference
Chain Reactions							
$\text{H} + \text{O}_2 = \text{O} + \text{OH}$	16.77	14.28	0.00	16.44	2	962-2577	Pirraglia, <i>et al.</i> , (1988)
$\text{O} + \text{H}_2 = \text{H} + \text{OH}$	1.85	4.71	2.67	6.29	1.5	297-2495	Sutherland, <i>et al.</i> , (1986)
$\text{OH} + \text{H}_2 = \text{H} + \text{H}_2\text{O}$	-15.01	8.33	1.51	3.43	1.5	250-2581	Michael and Sutherland, (1986)
$\text{OH} + \text{OH} = \text{O} + \text{H}_2\text{O}$	-16.88	$k = 5.46 \times 10^{10} \exp(0.00149 \times T)$			2.5	250-2000	Tsang and Hampson, (1986)
Dissociation/Recombination Reactions							
$\text{H}_2 = \text{M} + \text{H} + \text{H} + \text{M}(\text{N}_2)^a$	104.2	19.66	-1.40	104.38	3	600-2000	Tsang and Hampson, (1986)
$\text{H}_2 = \text{M} + \text{H} + \text{H} + \text{M}(\text{Ar})^b$	104.2	18.77	-1.10	104.38	2	600-5000	Tsang and Hampson, (1986)
$\text{O} + \text{O} = \text{M} + \text{O}_2 + \text{M}(\text{N}_2)$	-119.1	15.79	-0.50	0.00	1.3	2000-10000	Tsang and Hampson, (1986)
$\text{O} + \text{O} = \text{M} + \text{O}_2 + \text{M}(\text{Ar})$	-119.1	13.28	0.00	-1.79	1.3	2000-4000	Tsang and Hampson, (1986)
$\text{O} + \text{H} + \text{M} = \text{OH} + \text{M}$	-102.3	18.67	-1.00	0.00	10		Tsang and Hampson, (1986)
$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}(\text{N}_2)$	-119.2	22.35	-2.00	0.00	2	1000-3000	Tsang and Hampson, (1986)
$\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}(\text{Ar})$	-119.2	21.92	-2.00	0.00	2	1000-3000	Tsang and Hampson, (1986)
Formation and Consumption of HO <sub>2</sub>							
$\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}(\text{N}_2)$	-49.10	19.83	-1.42	0.00	3	200-2000	Slack, (1977)
$\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}(\text{Ar})$	-49.10	15.18	0.00	-1.00	2	300-2000	Baulch, <i>et al.</i> , (1973)
$\text{HO}_2 + \text{H} = \text{H}_2 + \text{O}_2$	-55.10	13.82	0.00	2.13	2	298-773	Tsang and Hampson, (1986)
$\text{HO}_2 + \text{H} = \text{OH} + \text{OH}$	-36.47	14.23	0.00	0.87	2	298-773	Tsang and Hampson, (1986)
$\text{HO}_2 + \text{O} = \text{OH} + \text{O}_2$	-53.23	13.24	0.00	0.40	1.2	200-400	Tsang and Hampson, (1986)
$\text{HO}_2 + \text{OH} = \text{H}_2\text{O} + \text{O}_2$	70.11	16.16	-1.00	0.00	2	298-1400	Tsang and Hampson, (1986)
Formation and Consumption of H <sub>2</sub> O <sub>2</sub>							
$\text{HO}_2 + \text{HO}_2 = \text{H}_2\text{O}_2 + \text{O}_2$	-38.53	12.48	0.00	1.39	3	650-800	Baldwin, <i>et al.</i> , (1986)
$\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}(\text{N}_2)$	51.17	17.08	0.00	45.50	2	700-1500	Warnatz, (1985)
$\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}(\text{Ar})$	51.17	16.93	0.00	45.50	2	700-1500	Warnatz, (1985)
$\text{H}_2\text{O}_2 + \text{H} = \text{H}_2\text{O} + \text{OH}$	-68.05	13.00	0.00	3.59	3	283-800	Warnatz, (1985)
$\text{H}_2\text{O}_2 + \text{H} = \text{H}_2 + \text{HO}_2$	-16.57	13.68	0.00	7.95	5	283-800	Tsang and Hampson, (1986)
$\text{H}_2\text{O}_2 + \text{O} = \text{OH} + \text{HO}_2$	-14.70	6.98	2.00	3.97	3	250-800	Tsang and Hampson, (1986)
$\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{HO}_2$	-31.58	12.85	0.00	1.43	2	298-800	Warnatz, (1985)
Formation of CO							
$\text{CO} + \text{O} = \text{M} + \text{CO}_2 + \text{M}(\text{N}_2)$	-127.18	13.40	0.00	-4.54	4	1000-3000	Warnatz, (1985)
$\text{CO} + \text{O} = \text{M} + \text{CO}_2 + \text{M}(\text{Ar})$	-127.18	13.34	0.00	-4.54	4	1000-3000	Warnatz, (1985)
$\text{CO} + \text{O}_2 = \text{CO}_2 + \text{O}$	8.08	12.40	0.00	47.69	2	1500-3000	Tsang and Hampson, (1986)
$\text{CO} + \text{OH} = \text{CO}_2 + \text{H}$	-24.85	$k = 6.75 \times 10^{10} \exp(0.000907 \times T)$			1.5	250-2500	Baulch, <i>et al.</i> , (1976)
$\text{CO} + \text{HO}_2 = \text{CO}_2 + \text{OH}$	-61.31	13.78	0.00	22.95	3	700-1000	Attri, <i>et al.</i> , (1986)
Formation and Consumption of HCO							
$\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}(\text{N}_2)$	15.28	17.27	1.0	17.00	5	637-832	Timonen, <i>et al.</i> , (1987a)
$\text{HCO} + \text{M} = \text{H} + \text{CO} + \text{M}(\text{Ar})$	15.28	17.27	-1.0	17.00	5	637-832	Timonen, <i>et al.</i> , (1987a)
$\text{HCO} + \text{O}_2 = \text{CO} + \text{HO}_2$	-33.82	12.88	0.00	0.41	5	295-713	Timonen, <i>et al.</i> , (1988)
$\text{HCO} + \text{H} = \text{CO} + \text{H}_2$	-88.92	13.86	0.00	0.00	2	296-418	Timonen, <i>et al.</i> , (1987b)
$\text{HCO} + \text{O} = \text{CO} + \text{OH}$	-87.05	13.48	0.00	0.00	3		Tsang and Hampson, (1986)
$\text{HCO} + \text{OH} = \text{CO} + \text{H}_2\text{O}$	-103.93	13.48	0.00	0.00	3		Tsang and Hampson, (1986)

<sup>a</sup>  $M = \sum_i \varepsilon_i [i]$  where  $\varepsilon_i$  = chaparron efficiency for species  $i$ ,  $\varepsilon_{\text{N}_2} = 1$ ,  $\varepsilon_{\text{H}_2} = 2.5$ ,  $\varepsilon_{\text{H}_2\text{O}} = 12.0$ ,  $\varepsilon_{\text{CO}} = 1.9$ ,  $\varepsilon_{\text{CO}_2} = 3.8$ ,  $\varepsilon_{\text{Ar}} = 0.75$ , all other species have efficiencies equal to unity.  
<sup>b</sup> With Ar as the bath gas, the chaparron efficiencies for the species listed above are scaled such that  $\varepsilon_{\text{Ar}} = 1$ , all species not listed have efficiencies equal to unity.  
<sup>c</sup> An alternate expression is provided in the text.

## Non-Elementary Reactions (II)

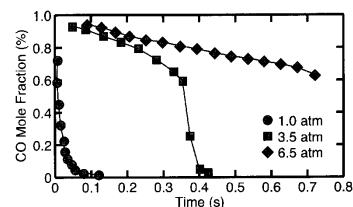
Using an overall rate expression for non-elementary reactions may lead to erroneous results – especially when extrapolated outside the concentration-temperature region for which the rate expression was derived, for example:



$$-r_{\text{CO}} = k_{\text{CO}} \cdot y_{\text{CO}} \cdot y_{\text{O}_2}^{1/4} \cdot y_{\text{H}_2\text{O}}^{1/2} \cdot P^{1.75}$$

Why does water enter the rate expression?

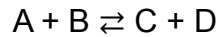
What effect of pressure on the rate would you expect from the rate expression?



Laboratory flow reactor experiments on carbon monoxide oxidation as function of [226]. The initial temperature is 1040 K and the initial mole fractions are 1.0% O<sub>2</sub>, and 0.65% H<sub>2</sub>O, with the balance N<sub>2</sub>.

## Reversible Elementary Reactions

Most reactions may be virtually irreversible at lower temperatures, but reversible at high temperatures.



The forward rate is:  $r_{A,forward} = -k_A \cdot C_A \cdot C_B$

The reverse rate is:  $r_{A,reverse} = k_{-A} \cdot C_C \cdot C_D$

The equilibrium constant is:  $K_C = \frac{C_{Ceq} \cdot C_{Deq}}{C_{Aeq} \cdot C_{Beq}} = \frac{k_A}{k_{-A}}$

The net rate of A disappearance is:

$$\begin{aligned} -r_{A,net} &= k_A \cdot C_A \cdot C_B - k_{-A} \cdot C_C \cdot C_D \\ &= k_A \cdot \left( C_A \cdot C_B - \frac{k_{-A}}{k_A} \cdot C_C \cdot C_D \right) = k_A \cdot \left( C_A \cdot C_B - \frac{C_C \cdot C_D}{K_C} \right) \end{aligned}$$

## Exercise

Calculate the concentration profile w.r.t. time in a constant volume batch reactor for the following rate expression:

$$-r_A = 1.0 \cdot C_A^{1.5} \frac{\text{mol A}}{\text{m}^3 \cdot \text{min}}$$

The initial concentration is  $C_{A0} = 1 \text{ mol/m}^3$

What is the concentration in the vessel after 2 minutes ?

Do the calculation by hand and using Maple.